

#### PATENT COOPERATION TREATY

PCT

**NOTIFICATION OF ELECTION**

## From the INTERNATIONAL BUREAU

To

Commissioner  
US Department of Commerce  
United States Patent and Trademark  
Office, PCT  
2011 South Clark Place Room  
CP2/5C24  
Arlington, VA 22202  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 26 April 2001 (26.04.01)	Arlington, VA 22202 <b>ETATS-UNIS D'AMERIQUE</b> in its capacity as elected Office
International application No. PCT/JP00/05487	Applicant's or agent's file reference 00-020-PCT
International filing date (day/month/year) 17 August 2000 (17.08.00)	Priority date (day/month/year) 20 August 1999 (20.08.99)
Applicant SAITO, Jun et al	

- 1. The designated Office is hereby notified of its election made:**

in the demand filed with the International Preliminary Examining Authority on:

12 March 2001 (12.03.01)

in a notice effecting later election filed with the International Bureau on:

2. The election  was

11

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p><b>The International Bureau of WIPO</b>  <b>34, chemin des Colombettes</b>  <b>1211 Geneva 20, Switzerland</b></p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p><b>Authorized officer</b></p> <p><b>R. Forax</b></p> <p>Telephone No.: (41-22) 338.83.38</p>
---	---

## ATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>00-020-PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT / JP 00 / 05487</b>	International filing date (day/month/year) <b>17/08/2000</b>	(Earliest) Priority Date (day/month/year) <b>20/08/1999</b>
Applicant <b>KAO CORPORATION</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
  - the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
  - contained in the international application in written form.
  - filed together with the international application in computer readable form.
  - furnished subsequently to this Authority in written form.
  - furnished subsequently to this Authority in computer readable form.
  - the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.  **Certain claims were found unsearchable (See Box I).**

3.  **Unity of Invention is lacking (see Box II).**

**4. With regard to the title,**

- the text is approved as submitted by the applicant.
- the text has been established by this Authority to read as follows:

**PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS**

**5. With regard to the abstract,**

- the text is approved as submitted by the applicant.
- the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

**6. The figure of the drawings to be published with the abstract is Figure No.**

- as suggested by the applicant.
- because the applicant failed to suggest a figure.
- because this figure better characterizes the invention.

None of the figures.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number  
**WO 01/14511 A1**

(51) International Patent Classification<sup>7</sup>: C11D 11/00,  
17/06, 3/12

1334, Minato, Wakayama-shi, Wakayama 640-8580 (JP).  
YAMASHITA, Hiroyuki [JP/JP]; Kao Corporation,  
Research Laboratories, 1334, Minato, Wakayama-shi,  
Wakayama 640-8580 (JP). SAKATA, Yushi [JP/JP];  
Kao Corporation, Research Laboratories, 1334, Minato,  
Wakayama-shi, Wakayama 640-8580 (JP).

(21) International Application Number: PCT/JP00/05487

(22) International Filing Date: 17 August 2000 (17.08.2000)

(25) Filing Language: English

(74) Agent: HOSODA, Yoshinori; Hosoda International  
Patent Office, Otemae M2 Building, 8-1, Tanimachi  
2-chome, Chuo-ku, Osaka-shi, Osaka 540-0012 (JP).

(26) Publication Language: English

(81) Designated States (national): CN, ID, US.

(30) Priority Data:  
11/234155 20 August 1999 (20.08.1999) JP

(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

(71) Applicant (for all designated States except US): KAO  
CORPORATION [JP/JP]; 14-10, Nihonbashi Kayabacho  
1-chome, Chuo-ku, Tokyo 103-8210 (JP).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventors; and

(75) Inventors/Applicants (for US only): SAITO, Jun [JP/JP];  
Kao Corporation Research Laboratories, 1334, Minato,  
Wakayama-shi, Wakayama 640-8580 (JP). NITTA, Hide-  
ichi [JP/JP]; Kao Corporation, Research Laboratories,

**WO 01/14511 A1**

(54) Title: PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS

(57) Abstract: A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of (A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and (B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture; and a process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of (a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and (b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

DESCRIPTION

## PROCESS FOR PREPARING HIGH-BULK DENSITY DETERGENT COMPOSITIONS

5

TECHNICAL FIELD

The present invention relates to a process for preparing a high-bulk density detergent composition having excellent detergency, and a small average particle size.

10

BACKGROUND ART

Processes for preparing powder detergents having a relatively high bulk density have been remarked.

Japanese Patent Laid-Open No. Hei 3-33199 discloses a method of producing a detergent composition comprising the steps of dry-neutralizing components in a high speed mixer/granulator at a temperature of 55°C or less, and thereafter adding a liquid binder thereto to carry out granulation. In addition, Japanese Patent Laid-Open No. Hei 4-363398 discloses a method of producing a detergent composition comprising the steps of dry-neutralizing components in a high speed mixer/granulator at a temperature of 55°C or more, and then adding a liquid binder thereto to carry out granulation.

In the processes as represented in the above publications, there are disclosed techniques for neutralizing an acid precursor of an anionic surfactant in the presence of an alkali metal aluminosilicate. However, the present inventors have found that there arise problems that the deterioration and the aggregation of

the alkali metal aluminosilicate take place by these techniques, so that the detergency of the detergent composition is lowered.

In view of eliminating the above problems, an object of the present invention is to provide a process for preparing a high-bulk density detergent composition having excellent detergency, and a small average particle size.

The above object and other objects of the present invention will be apparent from the following description.

#### DISCLOSURE OF INVENTION

10 The present invention relates to:

[1] a process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

(B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture; and

[2] a process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

(a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in

an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

- (b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

5

#### BEST MODE FOR CARRYING OUT THE INVENTION

The process for preparing a high-bulk density detergent composition of the present invention is roughly classified into the following two embodiments.

10

##### [Embodiment 1]

A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

- (A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and
- (B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture.

##### [Embodiment 2]

25 A process for preparing a high-bulk density detergent composition having

a bulk density of 650 g/L or more, comprising the steps of:

- (a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and
- (b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

10 1. Step (A) or Step (a)

Step (A) or step (a) is a step in which essentially the same operations are carried out.

The liquid acid precursor of an anionic surfactant usable in step (A) or step (a) refers to those anionic surfactants in the form of acids in a liquid or pasty state at room temperature or with heating, which are formed into salts by neutralization reaction. The liquid acid precursor of an anionic surfactant includes linear alkylbenzenesulfonic acids (LAS),  $\alpha$ -olefin sulfonic acids (AOS), alkyl sulfuric acids (AS), internal olefin sulfonic acids, sulfonic acids of fatty acid esters, alkylether sulfuric acids, dialkyl sulfosuccinic acids, and the like.

20 The liquid acid precursors may be used in a combination of two or more components.

The amount of the liquid acid precursor of an anionic surfactant can be appropriately set depending upon the composition of the desired detergent composition. The amount of the liquid acid precursor of an anionic surfactant, as an anionic surfactant formed by the neutralization reaction, is preferably from 5

to 55% by weight, more preferably from 5 to 45% by weight, still more preferably from 10 to 40% by weight especially preferably from 20 to 40% by weight, of the final high-bulk density detergent composition. Incidentally, the present invention is effective also in a case where the main surfactant is supplied  
5 in another form in the detergent composition.

The water-soluble, alkali inorganic substance usable in step (A) or step (a) exhibits an alkaline property which can neutralize the liquid acid precursor of an anionic surfactant. The water-soluble, alkali inorganic substance described above includes sodium carbonate, sodium hydrogencarbonate, sodium silicate, potassium carbonate, calcium carbonate, and the like. Among the water-soluble, alkali inorganic substances, preference is given to sodium carbonate because the sodium carbonate can act as a detergent builder and an alkalizing agent in the final detergent composition. Therefore, it is preferable to add the water-soluble, alkali inorganic substances in step (A) or step (a) in an amount equal to or  
10 exceeding in an amount necessary for neutralizing the liquid acid precursor of an anionic surfactant. For instance, the water-soluble, alkali inorganic substance is added in an amount of preferably from 1 to 20 times the equivalent amount required for neutralization of the liquid acid precursor of an anionic surfactant, more preferably from 2 to 15 times the equivalent amount required for  
15 neutralization, especially preferably from 3 to 15 times the equivalent amount required for neutralization.

The water-soluble, alkali inorganic substance is preferably granular, and its average particle size is preferably 30  $\mu\text{m}$  or more, more preferably from 40 to 200  $\mu\text{m}$ , most preferably from 50 to 100  $\mu\text{m}$ , from the viewpoints of the yield  
20 improvements and the storage stability. Here, the average particle size of the  
25

granular, water-soluble, alkali inorganic substance is evaluated based on volume, wherein the average particle size is measured by using a laser diffraction particle size distribution analyzer ("LA-700," commercially available from HORIBA Ltd.).

5 In step (A) or step (a), the mixing operation is carried in the substantial absence of the alkali metal aluminosilicate. Here, the phrase "the substantial absence of the alkali metal aluminosilicate" refers to a case where the content of the alkali metal aluminosilicate in step (A) or step (a) is preferably 5% by weight or less, more preferably 3% by weight or less, of the neutralization mixture in  
10 step (A) or step (a). When the alkali metal aluminosilicate exists in a large amount in step (A) or step (a), the deterioration and the aggregation of the alkali metal aluminosilicate by the contact with a liquid acid precursor of an anionic surfactant in an acid form take place, so that the detergency performance in the resulting detergent composition is likely to be lowered thereby. Therefore, the  
15 above problem can be eliminated by carrying out the mixing operation under specified conditions of the substantial absence of the alkali metal aluminosilicate.

Incidentally, as detailed below, Embodiment 1 also encompasses an embodiment where the addition of the alkali metal aluminosilicate of step (B) is initiated at during the course of the neutralization process of step (a), or at a point  
20 where the amount of the liquid acid precursor of an anionic surfactant added exceeds a certain level.

In step (A) or step (a), besides the water-soluble, alkali inorganic substance and the liquid acid precursor of an anionic surfactant, a part or all of optional ingredients can be added. Optional ingredients which can be blended at  
25 this step include, for instance, fluorescers, pigments, anti-redeposition agents

(polycarboxylate polymers, sodium salt of carboxymethyl cellulose, and the like); surfactants (fatty acids or salts thereof, linear alkylbenzenesulfonates, alkyl sulfates, and the like); diatomaceous earth, calcite, kaolin, bentonite, tripolyphosphates, sodium sulfate, sodium sulfite, and the like.

5        In the case where a detergent composition comprising a tripolyphosphate as a main builder component is prepared, the average particle size of the tripolyphosphates is not particularly limited, and the average particle size is preferably from 1 to 30  $\mu\text{m}$ , more preferably from 5 to 20  $\mu\text{m}$ , still more preferably from 6 to 15  $\mu\text{m}$ . From the viewpoint of inhibiting the aggregation of  
10      the detergent granules, the smaller the average particle size of the tripolyphosphate, the smaller the average particle size of the detergent granules. From the viewpoint of the productivity for preparing the detergent granules with small particle sizes on an industrial scale, the average particle size of the tripolyphosphate is preferably 1  $\mu\text{m}$  or more, and from the viewpoint of  
15      inhibiting the aggregation of the detergent granules, the average particle size is preferably 30  $\mu\text{m}$  or less. Here, the average particle size of the tripolyphosphate as referred to in the present specification is evaluated based on volume, wherein the average particle size is measured by using a laser diffraction particle size distribution analyzer ("LA-700," commercially available from HORIBA Ltd.).

20       The optional ingredients which are added in step (A) or step (a) are preferably those in a granular or powdery state, and those prepared by pulverizing a lumpy mass, or those which are separately granulated may be used. The average particle size of the optional ingredients is preferably 200  $\mu\text{m}$  or less. Incidentally, the optional ingredients may be added as an aqueous solution, paste  
25      or slurry. However, in order to prevent excessive aggregation, when water is

contained, its amount is preferably adjusted so as not to exceed the water content described below.

When the above optional ingredients are added, it is preferable that the optional ingredients are previously blended with the water-soluble, alkali inorganic substance before neutralizing in step (A) or step (a). The extent of mixing is preferably such that each of the ingredients is uniformly mixed. For instance, when an agitation granulator is used, it is preferable that the operation conditions for the agitation granulator are, for instance, a mixing time period of within 5 minutes.

In step (A) or step (a), water may be added for the purpose of accelerating the neutralization reaction. The amount of water added is preferably from 0.2 to 3 parts by weight, more preferably from 0.5 to 1.5 parts by weight, based on 100 parts by weight of the water-soluble, alkali inorganic substance (and in a case where optional ingredients are added, their weights on dry basis are added) in step (A) or step (a). The amount of water is preferably 0.2 parts by weight or more, from the viewpoint of initiating the neutralization reaction, and the amount is preferably 3 parts by weight or less, from the viewpoint of suppressing the aggregation of the detergent granules. Incidentally, in a case where water is contained in the components such as the liquid acid precursor of an anionic surfactant, or other water-soluble raw materials are used, or powder raw materials containing water are used, the amount of water to be added may be determined in consideration of these water contents.

In addition, as a more preferable embodiment for accelerating the neutralization reaction, an aqueous alkali solution or an alkali slurry solution (hereinafter simply referred to as "alkali solution") can be preferably used in

place of water mentioned above. By using the alkali solution, not only the neutralization reaction can be more accelerated as compared to the case of using water, but also the particle size of the resulting detergent granules can be made small, whereby the bulk density can be markedly increased.

5       The alkali solution is added in an amount of preferably from 0.05 to 0.5 times the equivalent amount required for neutralization of the liquid acid precursor of an anionic surfactant, more preferably from 0.10 to 0.45 times the equivalent amount required for neutralization, especially preferably from 0.10 to 0.40 times the equivalent amount required for neutralization. From the  
10      viewpoint of initiating the neutralization reaction to obtain desired effects, the amount is preferably 0.05 times or more the equivalent amount required for neutralization, and from the viewpoint of suppressing the aggregation of the detergent granules, the amount is preferably 0.5 times or less the equivalent amount required for neutralization. Incidentally, in a case where the alkali  
15      solution has a low concentration, an excess amount of water is supplied to the mixture along with the addition of a given amount of the alkali solution, so that the aggregation of the detergent granules is likely to take place. Therefore, the concentration of the alkali solution is preferably from 20 to 50% by weight, more preferably from 30 to 50% by weight, especially preferably from 40 to 50% by  
20      weight.

      In addition, the kinds of the alkalizing agent used in the alkali solution include strongly alkali aqueous solutions, such as aqueous sodium hydroxide and aqueous potassium hydroxide, which can readily cause the neutralization reaction with the liquid acid precursor of an anionic surfactant. Among them,  
25      the aqueous sodium hydroxide is favorably used from the viewpoint of costs.

The alkali aqueous solution more preferably has a pH of 12 or more, and it is preferable that the alkali solution is added by spraying or dropping to an extent that the alkali solution uniformly disperses when added. It is preferable that the alkali solution is added to a mixture of a water-soluble, alkali inorganic substance and other optional ingredients before blending with the liquid acid precursor of an anionic surfactant.

When the neutralization reaction is carried out in step (A) or step (a), it is preferable to previously add an inorganic acid, for example, sulfuric acid, and the like, to the liquid acid precursor of an anionic surfactant. In the granules obtained by neutralization reaction of a powdery or granular, water-soluble, alkali inorganic substance by using the mixture prepared by previously mixing the inorganic acid with the liquid acid precursor of an anionic surfactant, since a neutralized salt derived from the inorganic acid is present more near the granular surface than in the inner portion of the granules, the resulting granules have low adhesiveness and small particle sizes, whereby the granules having a high surfactant content can be prepared without causing the aggregation of the granules. In addition, since the granules obtainable in the manner described above have a large number of micropores, the granules having a high content of liquid ingredients, such as a nonionic surfactant, can be prepared. The inorganic acid is added in an amount of preferably from 0.1 to 1.0 moles, more preferably from 0.1 to 0.8 moles, still more preferably from 0.15 to 0.75 moles, especially preferably from 0.2 to 0.7 moles, most preferably from 0.25 to 0.65 moles, per one mol of the liquid acid precursor of an anionic surfactant. It is preferable that the inorganic acid is added in an amount of 0.1 moles or more, per one mol of the liquid acid precursor, from the viewpoint of suppressing the formation of

coarse grains of the detergent granules, and that the inorganic acid is added in an amount of preferably 1.0 mole or less, per one mol of the liquid acid precursor, from the viewpoint of securing the degree of freedom in the formulation composition of the concentrated detergent.

5 In step (A) or step (a), the order of adding the liquid acid precursor of an anionic surfactant and the water-soluble, alkali inorganic substance is not particularly specified. It is preferable that the liquid acid precursor is added to the water-soluble, alkali inorganic substance.

10 The method of adding the liquid acid precursor of an anionic surfactant may be carried out continuously or in a plurality of batches, and the plural addition means may be provided.

15 It is preferable that the neutralization process in step (A) or step (a) is carried out by using an agitation granulator. It is preferred that the agitation granulators are equipped with agitation blades and a chopper for disintegration and dispersion (or those replaced with a functionally equivalent means).

Concrete examples of the agitation granulators usable in the present invention for a batch process include Vertical Granulator (commercially available from Powrex Corp.); High-Speed Mixer (commercially available from Fukae Powtec Kogyo Corp.); Lödige Mixer (commercially available from Matsuzaka Giken Co., Ltd.); and PLOUGH SHARE Mixer (commercially available from PACIFIC MACHINERY & ENGINEERING Co., LTD.); Gericke Mixer (commercially available from Meiji Machine Co., Ltd.), and the like, and the Lödige Mixer and the PLOUGH SHARE Mixer are especially preferable. Concrete examples of the agitation granulators usable for a continuous process include continuous Lödige Mixer (moderate speed mixer).

those having relatively long residence time); high-speed mixer (those having relatively short residence time) such as CB recycler (commercially available from Lödige); Turbilizer (commercially available from Hosokawa Micron Corporation); Shugi Mixer (commercially available from Powrex Corp.); Flow Jet Mixer (commercially available from Funken Powtechs, Inc.), and the like.

5 Incidentally, in the present invention, the above mixers may be appropriately used in combination. For instance, the neutralization reaction by the blending of the water-soluble, alkali inorganic substance and other optional ingredients and the neutralization reaction by the addition of the liquid acid precursor of an

10 anionic surfactant may be treated in different agitation granulators.

It is more preferred that the agitation granulator used in the present invention is equipped with a jacket for adjusting the internal temperature of the granulator or is equipped with a nozzle for blowing a gas into the agitation granulator. Concrete examples of the more preferable agitation granulators include those mixers disclosed in Japanese Patent Laid-Open Nos. Hei 15 10-296064 and Hei 10-296065.

In addition, in step (A) or step (a), it is preferred that the neutralization is carried out while blowing a gas into an agitation granulator. By blowing a gas into the agitation granulator, the excess water produced in the neutralization reaction can be evaporated and the resulting granular product can be cooled with the gas, to thereby inhibit the granular product from forming into a doughy mass. The gases which may be usable include an N<sub>2</sub> gas, air, and the like. The amount of gas blown (amount of gas flow) is not particularly limited. The gas is blown at a rate of preferably equal to or greater than 0.002 parts by weight per minute, 20 more preferably equal to or greater than 0.02 parts by weight per minute, based 25

on 100 parts by weight of the granular product.

The mixture comprising the neutralization substance of the acid precursor of an anionic surfactant obtainable in step (A) or step (a) as described above (in step (A), however, a non-neutralized acid precursor of an anionic surfactant can be also included), and the remaining water-soluble, alkali inorganic substance and other optional ingredients (hereinafter referred to as "neutralization mixture") is in a powdery or lumpy state. Especially when a detergent containing a surfactant in a ratio exceeding 20% by weight to the final detergent composition is prepared, the detergent granules are likely to form coarse grains or become lumpy, so that it is preferable to provide a disintegration process for the purpose of obtaining a detergent composition having a small particle size. Concretely, when the content of the anionic surfactant is 30% by weight or more, of the neutralization mixture, it is preferable to provide the disintegration process.

The method for disintegration may be carried out subsequently to step (A) or step (a) in the agitation granulator equipped with agitation blades and a chopper for disintegration and dispersion, or the method may be carried out by a separate disintegrator. Concrete examples of the disintegrator include Fitz Mill (commercially available from Hosokawa Micron Corporation), Speed Mill (commercially available from Okada Seiko K.K.), and the like.

2. Step (B) or step (b)

2-1. Step (B)

Step (B) comprises adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of a neutralization mixture obtained during a course of a neutralization process in

step (A) and mixing a resulting mixture. By initiating the addition of the inorganic powder at this point, there can be exhibited an effect of accelerating the disintegration effect of the neutralization mixture.

It is desired that the addition of the inorganic powder is initiated at any time after a point when the liquid acid precursor of an anionic surfactant is added in an amount exceeding a weight ratio of 0.25, preferably an amount exceeding a weight ratio of 0.3, to the water-soluble, alkali inorganic substance. This is because the formation of coarse grains of the neutralization mixture is initiated at this point. Further, from the viewpoint of suppressing the compactification and the formation of coarse grains of the neutralization mixture by the progress of the granulation after the termination of the neutralization, it is desired that the inorganic powder is added within a short time period from the termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant, for instance, within 5 minutes. Within the above range, the disintegration of the neutralization mixture can be facilitated by initiating the addition of the inorganic powder within this range.

It is desired that the inorganic powder usable in step (B) has an average particle size of 30 µm or less, preferably 20 µm or less, from the viewpoint of suppressing the aggregation of the detergent granules. Here, the average particle size of the inorganic powder is evaluated based on volume, wherein the average particle size is measured by using a laser diffraction particle size distribution analyzer ("LA-700," commercially available from HORIBA Ltd.). Examples of the inorganic powder include inorganic powdery builders and fine granular components generally usable in detergent compositions. Concrete examples thereof include alkali metal aluminosilicates, tripolyphosphates, crystalline

silicates, sodium sulfate, calcite, diatomaceous earth, silica, and the like. The inorganic powders may be used in combination of two or more kinds. Among these inorganic powders, from the viewpoint of the disintegration efficiency, the alkali metal aluminosilicate is especially preferable.

5        The alkali metal aluminosilicate may be either amorphous or crystalline, and those having a metal ion capturing ability as a detergent aid are preferable, and especially those generally so-called "synthetic zeolite" in the field of detergent are preferable. The alkali metal aluminosilicate has an average particle size of preferably from 1 to 30 µm, more preferably from 10 µm or less.

10      Especially in step (B), in a case where the alkali metal aluminosilicate is added, it is preferable that the alkali metal aluminosilicate is added at any point after the termination of the addition of an entire amount of the liquid acid precursor of an anionic surfactant, preferably after any point between a point where the agitation granulator is operated for additional 30 seconds or more, 15 more preferably 1 minute or more, and a point up to 5 minutes from the termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant. By operating the agitation granulator after the termination of the addition of the liquid acid precursor, the neutralization reaction can be favorably completed. According to the above process, since the liquid acid precursor of an anionic surfactant is already neutralized, its deterioration and aggregation would not take place even if the alkali metal aluminosilicate were added. Therefore, the lowering of the detergency performance of the resulting detergent composition can be suppressed, so that there can be sufficiently exhibited an effect by the addition of the alkali metal aluminosilicate, namely the 20 effect of improving the metal ion capturing ability and the supporting ability of 25

the liquid ingredients.

2-2. Step (b)

Step (b) comprises adding an alkali metal aluminosilicate to a  
5 neutralization mixture obtained in step (a) and mixing a resulting mixture.

The neutralization mixture obtained in step (a) referred to herein is a  
mixture in which an entire amount of the liquid acid precursor of an anionic  
surfactant is added, and it is preferable those in which the neutralization is  
terminated. In addition, the alkali metal aluminosilicate usable in step (b) may  
10 be the same ones as those of step (B).

In step (b), it is preferable that the addition of the alkali metal  
aluminosilicate is initiated in step (b) at any time within 5 minutes from the  
termination of the addition of an entire amount of the liquid acid precursor of an  
anionic surfactant, from the viewpoint of suppressing the compactification and  
15 the formation of coarse grains of the neutralization mixture by the progress of the  
granulation after the termination of the neutralization process. Especially, it is  
preferable that the alkali metal aluminosilicate is added at any point after the  
termination of the addition of an entire amount of the liquid acid precursor of an  
anionic surfactant, preferably after any point between a point where the agitation  
20 granulator is operated for additional 30 seconds or more, more preferably  
1 minute or more, and a point up to 5 minutes from the termination of the  
addition of an entire amount of the liquid acid precursor of an anionic surfactant.  
By operating the agitation granulator after the termination of the addition of the  
liquid acid precursor, the neutralization reaction can be favorably completed.  
25 According to the above process, since the liquid acid precursor of an anionic

surfactant is already neutralized, its deterioration and aggregation would not take place even if the alkali metal aluminosilicate were added. Therefore, the lowering of the detergency performance of the resulting detergent composition can be suppressed, so that there can be sufficiently exhibited an effect by the 5 addition of the alkali metal aluminosilicate, namely the effect of improving the metal ion capturing ability and the supporting ability of the liquid ingredients.

### 2-3. Others

The amount of the inorganic powder usable in step (B) or the alkali metal 10 aluminosilicate usable in step (b) is preferably from 5 to 50% by weight, more preferably from 8 to 40% by weight, especially preferably from 10 to 36% by weight, of the high-bulk density detergent composition, which is the final product. From the viewpoint of suppressing the aggregation of the neutralization mixture, the amount is preferably 5% by weight or more, and from the viewpoint 15 of securing the degree of compositional freedom of the resulting detergent composition, the amount is preferably 50% by weight or less.

In addition, a method of adding an inorganic powder or alkali metal aluminosilicate includes adding it at once or in a plurality of divided portions. Embodiments for adding in a plurality of divided portions include (i) an 20 embodiment of adding an inorganic powder or alkali metal aluminosilicate for the purpose of facilitating disintegration when the neutralization mixture obtained in step (A) or step (a) is formed into coarse grains or lumpy masses (addition as a disintegration aid); (ii) an embodiment of adding an inorganic powder or alkali metal aluminosilicate for the purpose of adjusting the 25 granulation property when adding the liquid binder described below (addition as

a granulation adjustment agent); and (iii) an embodiment of adding an inorganic powder or alkali metal aluminosilicate before the surface modification of the finally obtained detergent granules (addition as a surface modifier).

In step (B) or step (b), from the viewpoints of the reduction of fine powder and the improvements in the detergency and the metal ion capturing ability, it is desirable to formulate a liquid binder. According to the process of the present invention, the neutralization mixture can be made to have a small particle size, so that greater amounts of the liquid binder can be formulated.

The term "liquid binder" in the present invention refers to a substance imparting a property of increasing the bulk density of the detergent composition by collectively assembling the granules by the formulation of the liquid binder. The liquid binder includes, for instance, optional liquid ingredients in the detergent composition such as water, liquid nonionic surfactants, aqueous solutions of water-soluble polymers (polyethylene glycols, acrylic acid-maleic acid copolymers, and the like), and fatty acids. These liquid binders may be used in combination of two or more kinds, and embodiments of such addition methods include (1) adding after previously mixing two or more liquid binders; (2) simultaneously adding each of the liquid binders; and (3) alternately adding each of the liquid binders. In any of these methods, from the viewpoints of cost reduction, it is preferable to use water in combination. The amount of the liquid binder formulated is preferably 20 parts by weight or less, more preferably 15 parts by weight or less, based on 100 parts by weight of the neutralization mixture, from the viewpoint of suppressing the aggregation of the detergent composition.

The method of adding the liquid binder may be carried out continuously

or in a plurality of batches. It is preferable that the liquid binder is added to the neutralization mixture obtained in step (A) or step (a) before or after the addition of the inorganic powder. By the addition of the liquid binder at this stage, the adhesiveness of the granular surface by the liquid binder can be reduced,  
5 whereby the granulation can be suppressed. In the process of the present invention, besides adding a part of or all of optional ingredients in step (A) or step (a), the optional ingredients can also be formulated in step (B) or step (b). Especially when the above aqueous solution of the water-soluble polymer is used, it is preferable to add the aqueous solution in step (B) or step (b) rather than in  
10 step (A) or step (a), from the viewpoint of granulation property. In this case, the inorganic powder can be added in plural batches as shown in the above embodiments (i) to (iii), so that the granulation property is not greatly affected by the water content carried by the optional ingredients into the neutralization mixture.

15 In the process of the present invention, it is preferable to provide a surface-modifying step as shown in the above embodiment (iii). The surface modification step can be also carried out by using the inorganic powder such as an alkali metal aluminosilicate. By adding the inorganic powder to detergent granules in which the granulation is proceeded to a certain extent and surface-coating the detergent granules, the powder properties such as anti-caking  
20 property and flowability can be improved.

It is desired that the amount of the surface modifier is from 2 to 15% by weight, preferably from 4 to 12% by weight, of the detergent composition after the surface modification.

25 Incidentally, in the present invention, in a case where other volatile

compounds or thermally sensitive optional ingredients are added, such components may be added after at a point where at least the first batch of the inorganic powder or alkali metal aluminosilicate is added in step (B) or step (b) in the present invention, and the particle sizes are evenly sized, or these 5 components may be after-blended by mixing the granules finally treated with a surface-coating agent by using a mixer such as a rotary mixer.

The high-bulk density detergent composition obtained by the process of the present invention may be used as ingredients for constituting other detergent compositions.

10 In addition, the process of the present invention can be carried out by a continuous process. In this case, step (A) or step (a) can be carried out using, for instance, a high-speed mixer such as CB recycler, and thereafter, step (B) or step (b) can be carried out using, for instance, a moderate-speed mixer such as continuous Lödige Mixer.

15 According to the process described above, a high-bulk density detergent composition comprising a granular mixture having a bulk density of 650 g/L or more, the detergent composition having excellent detergency and a small average particle size, can be obtained.

20 It is more preferable that the high-bulk density detergent composition obtained by the process of the present invention has the following properties.

Average particle size: Measured by vibrating a sample with each of standard sieves according to JIS Z 8801 for 5 minutes, and thereafter determining from a weight percentage depending upon the size openings of the sieves. The average particle size is preferably 700  $\mu\text{m}$  or less, more preferably 25 650  $\mu\text{m}$  or less.

Bulk density: Preferably from 650 to 950 g/L, more preferably from 700 to 900 g/L. Here, in the present specification, the bulk density is measured by a method according to JIS K 3362.

Flowability: The flowability of the detergent composition in the present specification is expressed as flow time which is defined as a time period required for dropping 100 mL of a powdery detergent composition from a hopper used in the determination of the bulk density according to JIS K 3362. The flow time is preferably 8 seconds or shorter, more preferably 7 seconds or shorter.

Detergency: The detergency is expressed a relative detergency ratio. The relative detergency ratio is preferably 0.95 or more, more preferably 0.98 or more. The more the relative detergency ratio approximates 1, the less the affect of the process to individual ingredients. Incidentally, in the present invention, the relative detergency ratio is obtained as follows.

First, a detergent composition to be tested is dissolved in water, to give an aqueous solution of the detergent composition. This solution is referred to as "test detergent aqueous solution." Next, an aqueous solution having the same composition as the test detergent aqueous solution is obtained by adding and mixing the individual ingredients constituting the detergent composition with water. This aqueous solution is referred to as "control detergent aqueous solution." The detergency of the test detergent aqueous solution and the detergency of the control detergent aqueous solution are obtained by the following detergency test. Thereafter, the relative detergency ratio is obtained by:

$$\text{Relative Detergency Ratio} = \frac{\text{Detergency of Test Detergent Aqueous Solution}}{\text{Detergency of Control Detergent Aqueous Solution}}$$

## &lt;Detergency of Detergent&gt;

## (Preparation of Artificial Stained Cloth)

An artificially stained cloth is prepared by smearing an artificial soil solution having the composition shown in Table 1 to a cloth. The smearing of the artificial soil solution to a cloth is carried out in accordance with Japanese Patent Laid-Open No. 7-270395 wherein the artificial soil solution was printed on a cloth by a gravure staining machine equipped with a gravure roll coater. The conditions for smearing the artificial soil solution to a cloth to prepare an artificially stained cloth are a cell capacity of a gravure roll of  $58 \text{ cm}^3/\text{cm}^2$ , a coating speed of 1.0 m/min, a drying temperature of 100°C, and a drying time of one minute. As to the cloths, #2003 calico (manufactured by Tanigashira Shoten) is used.

Table 1

Lauric Acid	0.44% by weight
Myristic Acid	3.09% by weight
Pentadecanoic Acid	2.31% by weight
Palmitic Acid	6.18% by weight
Heptadecanoic Acid	0.44% by weight
Stearic Acid	1.57% by weight
Oleic Acid	7.75% by weight
Triolein	13.06% by weight
n-Hexadecyl Palmitate	2.18% by weight
Squalene	6.53% by weight
Lecithin, from Egg White	1.94% by weight
Kanuma Red Clay	8.11 by weight
Carbon Black	0.01 by weight
Tap Water	Balance

## (Detergent Conditions and Evaluation Method)

Five pieces of the artificially stained cloths of 10 cm x 10 cm prepared above are placed in one liter of an aqueous solution for measurement detergent or that of control detergent and washed with turgotometer at 100 rotations/min. The washing conditions are concretely as follows: the washing time: 10 minutes, the detergent concentration: 0.083% by weight; water hardness: 5°DH; water temperature: 20°C; rinsing: with tap water for 5 minutes.

The detergency was evaluated by measuring the reflectance at 550 nm of the original cloth before staining and those of the stained cloth before and after washing by an automatic recording colorimeter (manufactured by SHIMADZU

CORPORATION), and the detergency (%) was calculated by the following equation. The average value determined of 5 pieces was expressed as the detergency (%).

$$\text{Detergency } (\%) = \frac{\frac{\text{Reflectance After Washing} - \text{Reflectance Before Washing}}{\text{Reflectance of Original Cloth} - \text{Reflectance Before Washing}}}{\times 100}$$

5

In the subsequent Examples, as the zeolite, there was used Zeolite 4A (manufactured by Tosoh Corporation); as the nonionic surfactant, there was used a polyoxyethylene alkyl ether (prepared by adding ethylene oxide in an average of 8 moles to a primary alcohol of which alkyl moiety has 12 to 14 carbon atoms 10 (average being 12.8)); as a fatty acid, there was used palmitic acid; and as the acrylic acid-maleic acid copolymer, there was used one having a weight-average molecular weight of about 70000 as determined by gel permeation method using a polyethylene glycol as a standard.

15 Example 1

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer was equipped with agitator blades; a shearing device corresponding to a chopper for 20 disintegration and dispersion; and a jacket for adjusting the temperature within the mixer.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 13.19 parts by weight of sodium carbonate ("LIGHT ASH," manufactured by Central Glass Co., Ltd.; average particle size: 56.1 µm), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the conditions of a rotational speed of agitator blades of 130 rotations/min (peripheral speed: 3.4 m/s) and a rotational speed of a shearing device of 2850 rotations/min (peripheral speed: 27 m/s).

10

<Neutralization>

While the mixer was operated under the same conditions as above, 9.40 parts by weight of a linear alkylbenzenesulfonic acid (LAS; molecular weight: 322) was added to the mixer in 4 minutes. During this stage, the 15 ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the LAS, the temperature inside the mixer rose to 75°C in the highest. After the addition of the LAS, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the 20 initiation of addition of the LAS, the aeration within the mixer (300 L/min) was carried out.

<Addition of Alkali Metal Aluminosilicate>

At a point where the neutralization reaction and granulation process were 25 completed, a zeolite (5.00 parts by weight) having an average particle size of

4  $\mu\text{m}$  was added, while the mixer was operated under the same conditions as above, and mixing was carried out for 5 minutes.

<Addition of Liquid Ingredients and Surface Modification>

5 While the mixer was operated under the same conditions as above, the nonionic surfactant (0.98 parts by weight) was added to the mixer and blended for one minute. Next, a zeolite (2.00 parts by weight) having an average particle size of 4  $\mu\text{m}$  was added thereto, and blended for additional 5 minutes. Thereafter, 10 a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to a surface modification treatment by adding the zeolite (3.50 parts by weight) having an average particle size of 4  $\mu\text{m}$  to the mixer as a surface modifier, and operating the mixer for additional one minute.

15 The granules of the resulting detergent composition had an average particle size of 640  $\mu\text{m}$ , a bulk density of 795 g/L, and a flowability of 7.1 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.998, whereby showing excellent detergency.

20

<After-Blending>

Using a rotary mixer, an enzyme (0.18 parts by weight) and the detergent composition obtained above were mixed, and a perfume (0.07 parts by weight) was further sprayed thereto, to give a final powder of the high-bulk density 25 detergent composition.

Example 2

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 12.88 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

15 <Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 9.40 parts of by weight of the LAS and 0.84 parts by weight of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 80°C in the highest. After the addition of the mixture, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

## &lt;Addition of Alkali Metal Aluminosilicate&gt;

In the same manner as in Example 1, a zeolite (5.00 parts by weight) having an average particle size of 4  $\mu\text{m}$  was added, and mixing was carried out  
5 for 5 minutes.

## &lt;Addition of Liquid Ingredients and Surface Modification&gt;

In the same manner as in Example 1, the nonionic surfactant (0.98 parts by weight), the zeolite (2.00 parts by weight) having an average particle size of  
10 4  $\mu\text{m}$ , and the 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) were added to the mixer, and the ingredients were blended. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average  
15 particle size of 565  $\mu\text{m}$ , a bulk density of 776 g/L, and a flowability of 7.3 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.988, whereby showing excellent detergency.

## 20 &lt;After-Blending&gt;

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

25 Example 3

A detergent composition was obtained by using the same composition and the operations as employed in Example 2, except for changing the amount of LIGHT ASH used to 12.73 parts by weight, adding 0.23 parts by weight of a 48% by weight aqueous NaOH solution as a reaction initiating agent before neutralization to the mixture of LIGHT ASH and a fluorescer, and thereafter adding a process for blending for 1 minute and 30 seconds under the same conditions as those for the process of powder blending.

The granules of the resulting detergent composition had an average particle size of 550 µm, a bulk density of 780 g/L, and a flowability of 7.3 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.990, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

Example 4

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows.

## &lt;Powder Blending&gt;

Solid ingredients, comprising 12.22 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

## 5 &lt;Neutralization&gt;

While the mixer was operated under the same conditions as above, a mixture comprising 7.39 parts by weight of the LAS and 0.87 parts by weight 10 of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 75°C in the highest. After the addition of the mixture, the mixer was continuously operated under the same conditions for 5 minutes to complete the 15 neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out. Subsequently, 0.97 parts by weight of a fatty acid was added in 30 seconds, and thereafter, the ingredients were mixed for one minute.

## 20 &lt;Addition of Alkali Metal Aluminosilicate&gt;

In the same manner as in Example 1, a zeolite (6.05 parts by weight) having an average particle size of 4 µm was added, and mixing was carried out 25 for 5 minutes.

<Addition of Liquid Ingredients and Surface Modification>

In the same manner as in Example 1, the nonionic surfactant (1.51 parts by weight), the zeolite (2.00 parts by weight) having an average particle size of 4 µm, and the 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) were added to the mixer, and the ingredients were blended. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average particle size of 510 µm, a bulk density of 778 g/L, and a flowability of 6.5 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.988, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

Example 5

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

Solid ingredients, comprising 11.00 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

5  
<Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 11.76 parts of by weight of the LAS and 1.05 parts by weight of 98% sulfuric acid was added to the mixer in 5 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 85°C in the highest. After the addition of the mixture, the mixer was continuously operated under the same conditions for 4 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

10  
15  
<Addition and Disintegration of Alkali Metal Aluminosilicate>

20 While the mixer was operated under the same conditions as above, a zeolite (5.00 parts by weight) having an average particle size of 4 µm was added as a disintegration aid, and mixing was carried out for 5 minutes. Thereafter, the mixture was disintegrated using a Fitz Mill (manufactured by Hosokawa Micron Corporation).

<Addition of Liquid Ingredients and Surface Modification>

While the disintegrated mixture was stirred in the above Lödige Mixer under the same conditions as above, the nonionic surfactant (0.70 parts by weight) was added to the mixer and blended for one minute. Next, a zeolite (2.00 parts by weight) having an average particle size of 4 µm was added thereto, and blended for additional 5 minutes. Thereafter, a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer (effective ingredient: 1.49 parts by weight) was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

The granules of the resulting detergent composition had an average particle size of 560 µm, a bulk density of 780 g/L, and a flowability of 7.4 seconds, whereby showing excellent powder properties. In addition, the granules had a relative ratio for the detergency rate of 0.994, whereby showing excellent detergency.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density detergent composition.

Comparative Example 1

A detergent composition having a composition shown in Table 2 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had

the same construction as that described in Example 1.

The operations were carried out as follows.

<Powder Blending>

5 Solid ingredients, comprising 13.19 parts by weight of sodium carbonate (the same "LIGHT ASH" as in Example 1), 7.00 parts by weight of a zeolite having an average particle size of 4 µm, and 0.11 parts by weight of a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

10

<Neutralization>

While the mixer was operated under the same conditions as above, 9.40 parts by weight of the LAS was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the LAS, the temperature inside the mixer rose to 75°C in the highest. After the addition of the LAS, the mixer was continuously operated under the same conditions for 5 minutes to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the LAS, the aeration within the mixer (300 L/min) was carried out.

15

20

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as above, the nonionic surfactant (0.98 parts by weight) was added to the mixer and blended for one minute, and thereafter a 40% by weight aqueous solution of acrylic acid-

25

maleic acid copolymer (effective ingredient: 1.49 parts by weight) was added to the mixer, and the ingredients were blended for 1 minute and 30 seconds. Subsequently, the resulting mixture was subjected to the same surface modification treatment as in Example 1.

5 The granules of the resulting detergent composition had an average particle size of 650 µm, a bulk density of 770 g/L, and a flowability of 6.9 seconds, whereby showing excellent powder properties. However, the granules had a relative ratio for the detergency rate of 0.902, whereby showing notably poorer detergency.

10

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the detergent composition.

Table 2

	Example No.					Comp. Ex. No.
	1	2	3	4	5	1
<b>Composition (% by weight)</b>						
LAS-Na	28.00	28.00	28.00	22.00	35.00	28.00
Soap	0.00	0.00	0.00	3.00	0.00	0.00
Zeolite	30.00	30.00	30.00	33.00	30.00	30.00
Sodium Carbonate	33.00	29.50	29.50	28.00	22.30	33.00
Sodium Sulfate	0.50	4.00	4.00	4.00	5.00	0.50
Copolymer*	1.70	1.70	1.70	1.70	1.70	1.70
Nonionic**	2.80	2.80	2.80	4.30	2.00	2.80
Fluorescer	0.30	0.30	0.30	0.30	0.30	0.30
Enzyme	0.50	0.50	0.50	0.50	0.50	0.50
Perfume	0.20	0.20	0.20	0.20	0.20	0.20
Water	3.00	3.00	3.00	3.00	3.00	3.00
Total	100.00	100.00	100.00	100.00	100.00	100.00

\*: Acrylic acid-maleic acid copolymer.

\*\*: Nonionic surfactant.

### Examples 6 to 8 and Comparative Example 2

5 A detergent composition having a composition shown in Table 3 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

The operations were carried out as follows (the amount of each raw material formulated in each step is shown in Table 4).

<Powder Blending>

Solid ingredients, comprising sodium carbonate ("LIGHT ASH,"  
5 manufactured by Central Glass Co., Ltd.; average particle size: 56.1 µm), sodium tripolyphosphate (STPP; average particle size: 11.2 µm), and a fluorescer, were blended for one minute with the above Lödige Mixer under the conditions of a rotational speed of agitator blades of 130 rotations/min (peripheral speed: 3.4 m/s) and a rotational speed of a shearing device of 2850 rotations/min  
10 (peripheral speed: 27 m/s).

<Addition of Reaction Initiating Agent>

A 48% by weight of NaOH aqueous solution was added to the contents in the mixer as a reaction initiating agent, and the blending was carried out for  
15 1 minute and 30 seconds under the same conditions as above.

<Neutralization>

While the mixer was operated under the same conditions as above, a mixture comprising 9.40 parts of by weight of the LAS and 0.84 parts by weight  
20 of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 75°C in the highest. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried  
25 out.

<Blending of Inorganic Powder >

An inorganic powder (1.75 parts by weight) was added to the resulting neutralized mixture, and the mixer was continuously operated under the same  
5 conditions as above for 4 minutes and 30 seconds.

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as above, the nonionic surfactant (0.98 parts by weight) was added to the mixer and blended  
10 for one minute. Next, a zeolite (2.00 parts by weight) having an average particle size of 4 µm was added thereto, and blended for additional 5 minutes. Thereafter,  
a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer was  
added to the mixer, and the ingredients were blended for 1 minute and 30  
seconds. Subsequently, the resulting mixture was subjected to a surface  
15 modification treatment by adding the zeolite (2.20 parts by weight) having an average particle size of 4 µm to the mixer as a surface modifier, and operating the mixer for additional one minute.

<After-Blending>

20 In the same manner as in Example 1, the enzyme and the perfume were added thereto, to give a final powder of the high-bulk density granular detergent composition.

25 Here, in Example 6 or 7, after 30 seconds from the termination of addition of the LAS, STPP or zeolite (1.75 parts by weight) was added as an inorganic

powder. In addition, in Example 8, the addition of STPP, an inorganic powder was carried out during the course of the neutralization process, and the mixture was continued to be blended for 5 minutes after termination of the addition of the LAS. Incidentally, the addition of STPP was carried out at a point where a  
5 weight ratio of the LAS added to sodium carbonate reached 0.6. In Comparative Example 2, the mixture was blended for 5 minutes after the termination of the addition of LAS, without adding an inorganic powder during the course of the neutralization process or immediately after the neutralization process.

10 The properties of each of the resulting high-density detergent composition are shown in Table 5.

Table 3

	Example No.				Comp. Ex. No. 2
	6	7	8	9	
<b>Composition (% by weight)</b>					
LAS-Na	28.00	28.00	28.00	28.00	28.00
Zeolite	12.00	17.00	12.00	12.00	12.00
STPP	20.00	15.00	20.00	20.00	20.00
Sodium Carbonate	27.50	27.50	27.50	28.80	27.50
Sodium Sulfate	4.00	4.00	4.00	4.00	4.00
Copolymer*	1.70	1.70	1.70	1.70	1.70
Nonionic**	2.80	2.80	2.80	—	2.80
Fluorescer	0.30	0.30	0.30	0.30	0.30
Enzyme	0.50	0.50	0.50	0.50	0.50
Perfume	0.20	0.20	0.20	0.20	0.20
Water	3.00	3.00	3.00	4.50	3.00
Total	100.00	100.00	100.00	100.00	100.00

\*: Acrylic acid-maleic acid copolymer.

\*\*: Nonionic surfactant.

Table 4

Composition (parts by weight)	Example No.				Comp. Ex. No. 2
	6	7	8	9	
<b>&lt;Powder Blending&gt;</b>					
Sodium Carbonate	12.03	12.03	12.03	12.48	12.03
Sodium Tripolyphosphate	5.25	5.25	5.25	5.25	7.00
Fluorescer	0.11	0.11	0.11	0.11	0.11
<b>&lt;Addition of Reaction Initiating Agent&gt;</b>					
48% by weight NaOH	0.23	0.23	0.23	0.23	0.23
<b>&lt;Neutralization&gt;</b>					
Linear Alkylbenzene-sulfonic Acid (LAS)	9.40	9.40	9.40	9.40	9.40
98% Sulfuric Acid (Amount of Air Flow [L/min])	0.84 300	0.84 300	0.84 300	0.84 300	0.84 300
<b>&lt;Blending of Inorganic Powder&gt;</b>					
Sodium Tripolyphosphate	1.75	—	1.75	—	—
Zeolite	—	1.75	—	3.75	—
<b>&lt;Addition of Liquid Ingredients and Surface Modification&gt;</b>					
Nonionic Surfactant	0.98	0.98	0.98	—	0.98
Zeolite	2.00	2.00	2.00	—	2.00
Water	—	—	—	0.53	—
Acrylic Acid-Maleic Acid Copolymer (Effective Ingredient)	1.49	1.49	1.49	1.49	1.49
Zeolite for Surface Modification	2.20	2.20	2.20	2.20	2.20
<b>&lt;After-Blending&gt;</b>					
Enzyme	0.18	0.18	0.18	0.18	0.18
Perfume	0.07	0.07	0.07	0.07	0.07

Table 5

	Example No.				Comp. Ex. No.
	6	7	8	9	
Final Average Particle Size ( $\mu\text{m}$ )	460	457	474	450	547
Average Particle Size ( $\mu\text{m}$ ) Immediately After Acid Addition	465	458	460	453	440
Bulk Density (g/L)	753	756	764	755	783
Flowability (sec)	6.5	6.5	6.5	6.4	6.7
Ratio of Relative Detergency	0.997	0.988	0.996	0.996	0.997

It is clear from the above results of Table 5 that by adding an inorganic powder during the course or immediately after the neutralization process, the granular growth from the termination of the neutralization process can be suppressed, and consequently, there can be obtained a high-bulk density detergent composition not only having excellent detergency but also comprising granules having a small average particle size.

10

#### Example 9

A detergent composition having a composition shown in Table 3 was prepared in an amount of 35 kg for each unit, using a Lödige Mixer "FKM-130D" (manufactured by Matsubo Co., Ltd.). This mixer basically had the same construction as that described in Example 1.

15

The operations were carried out as follows (the amount of each raw material formulated in each step is shown in Table 4).

<Powder Blending>

5 Solid ingredients, comprising sodium carbonate (the same LIGHT ASH as in Example 1), sodium tripolyphosphate (the same STPP as in Example 6), and a fluorescer, were blended for one minute with the above Lödige Mixer under the same conditions as in Example 1.

<Neutralization>

10 While the mixer was operated under the same conditions as in Example 1, a mixture comprising 9.40 parts by weight of the LAS and 0.84 parts by weight of 98% sulfuric acid was added to the mixer in 4 minutes. During this stage, the ingredients were cooled by allowing water at 25°C to flow through the mixer jacket. During the addition of the mixture, the temperature inside the mixer rose to 80°C in the highest. After the completion of the addition of the mixture, the mixer was continuously operated under the same conditions for 15 30 seconds to complete the neutralization reaction and the granulation operation. In addition, from immediately after the initiation of addition of the mixture, the aeration within the mixer (300 L/min) was carried out.

20

<Addition of Alkali Metal Aluminosilicate>

Zeolite (3.75 parts by weight) was added to the resulting neutralized mixture, and the mixer was continuously operated under the same conditions as above for 4 minutes and 30 seconds.

25

<Addition of Liquid Ingredients and Surface Modification>

While the mixer was operated under the same conditions as in Example 1, a mixture comprising a 40% by weight aqueous solution of acrylic acid-maleic acid copolymer and water was added to the mixer and blended for 1 minute and 5 30 seconds. Subsequently, the resulting mixture was subjected to a surface modification treatment in the same manner as in Example 1.

<After-Blending>

In the same manner as in Example 1, the enzyme and the perfume were 10 added thereto, to give a final powder of the high-bulk density granular detergent composition.

The properties of the resulting high-bulk density detergent composition are shown in Table 5. It is clear from Table 5 that a high-bulk density detergent 15 composition having excellent detergency and a small average particle size can be obtained.

INDUSTRIAL APPLICABILITY

According to the process of the present invention, a high-bulk density 20 detergent composition having excellent detergency and a small average particle size can be obtained.

## CLAIMS

1. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:
  - 5 (A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and
  - 10 (B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture.
- 15 2. The process according to claim 1, wherein the addition of the inorganic powder is initiated in step (B) at any time between a point when the liquid acid precursor of an anionic surfactant is added in an amount exceeding a weight ratio of 0.25 to the water-soluble, alkali inorganic substance and a point up to 5 minutes from termination of addition of an entire amount of the liquid acid precursor.
- 20 3. The process according to claim 1 or 2, wherein the average particle size of the inorganic powder is 30 µm or less.
- 25 4. The process according to any one of claims 1 to 3, wherein the inorganic

powder is an alkali metal aluminosilicate.

5. The process according to claim 4, wherein the addition of the alkali metal aluminosilicate is initiated in step (B) at any time within 5 minutes from

5 termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.

6. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

10 (a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

15 (b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

7. The process according to claim 6, wherein the addition of the alkali metal aluminosilicate is initiated in step (b) at any time within 5 minutes from

20 termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/05487

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C11D11/00 C11D17/06 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 936 269 A (KAO CORP) 18 August 1999 (1999-08-18) claims; examples 1,11-19 ---	1-7
X	WO 97 32003 A (PROCTER & GAMBLE) 4 September 1997 (1997-09-04) claims; examples ---	1-7
X	US 5 935 923 A (GUPTA ANSHU MALI) 10 August 1999 (1999-08-10) claims; examples ---	1,2,4-7
X	DE 197 35 788 A (HENKEL KGAA) 25 February 1999 (1999-02-25) example ---	1,2,4-7
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

7 November 2000

14/11/2000

Name and mailing address of the ISA  
 European Patent Office, P.B. 5818 Patenttaan 2  
 NL - 2260 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Pfannenstein, H

**INTERNATIONAL SEARCH REPORT**

Inte: nat Application No

PCT/JP 00/05487

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 11198 A (UNILEVER PLC ;UNILEVER NV (NL)) 19 March 1998 (1998-03-19) claims; examples ---	1,2,4-7
X	EP 0 352 135 A (UNILEVER PLC ;UNILEVER NV (NL)) 24 January 1990 (1990-01-24) cited in the application claims; examples 10-14,22,24,25 ---	1-7
X	DE 299 05 721 U (HENKEL KGAA) 22 July 1999 (1999-07-22) examples -----	1,2

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/JP 00/05487

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0936269	A	18-08-1999	CN	1235633 A	17-11-1999
			WO	9810052 A	12-03-1998
WO 9732003	A	04-09-1997	AU	5179496 A	16-09-1997
			BR	9612535 A	20-07-1999
			CZ	9802730 A	16-12-1998
			EP	0883678 A	16-12-1998
			HU	9901066 A	30-08-1999
			JP	2898102 B	31-05-1999
			JP	10505631 T	02-06-1998
US 5935923	A	10-08-1999	AU	4700697 A	02-04-1998
			BR	9711710 A	24-08-1999
			CN	1230215 A	29-09-1999
			WO	9811197 A	19-03-1998
			EP	0925353 A	30-06-1999
			ZA	9708145 A	10-03-1999
DE 19735788	A	25-02-1999	NONE		
WO 9811198	A	19-03-1998	AU	4700797 A	02-04-1998
			BR	9711714 A	24-08-1999
			CN	1235632 A	17-11-1999
			EP	0925354 A	30-06-1999
			ZA	9708144 A	10-03-1999
EP 0352135	A	24-01-1990	AU	611555 B	13-06-1991
			AU	3374989 A	02-11-1989
			AU	611556 B	13-06-1991
			AU	3375189 A	25-01-1990
			AU	612504 B	11-07-1991
			AU	3883889 A	25-01-1990
			BR	8902005 A	05-12-1989
			BR	8902006 A	10-04-1990
			BR	8903627 A	13-03-1990
			CA	1322704 A	05-10-1993
			CA	1323277 A	19-10-1993
			CA	1337513 A	07-11-1995
			DE	68907438 D	12-08-1993
			DE	68907438 T	14-10-1993
			DE	68912983 D	24-03-1994
			DE	68912983 T	01-06-1994
			DE	68918522 D	03-11-1994
			DE	68918522 T	09-03-1995
			EP	0339996 A	02-11-1989
			EP	0351937 A	24-01-1990
			ES	2043009 T	16-12-1993
			ES	2049320 T	16-04-1994
			ES	2063826 T	16-01-1995
			GB	2221695 A, B	14-02-1990
			HK	47894 A	20-05-1994
			HK	53292 A	24-07-1992
			HK	86594 A	02-09-1994
			HK	142995 A	15-09-1995
			IN	170472 A	28-03-1992
			IN	169824 A	28-12-1991
			IN	170991 A	27-06-1992
			JP	2049100 A	19-02-1990

# INTERNATIONAL SEARCH REPORT

...formation on patent family members

International Application No

PCT/JP 00/05487

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0352135	A	JP	7015119 B	22-02-1995
		JP	2041399 A	09-02-1990
		JP	2644038 B	25-08-1997
		JP	3033199 A	13-02-1991
		JP	6078558 B	05-10-1994
		KR	9200113 B	09-01-1992
		KR	9204462 B	05-06-1992
		KR	9200114 B	09-01-1992
		PH	26823 A	05-11-1992
		PH	25538 A	24-07-1991
		PH	26671 A	15-09-1992
		SG	38092 G	04-09-1992
		SG	98794 G	28-10-1994
		TR	25923 A	17-09-1993
		TR	25924 A	17-09-1993
		TR	27078 A	18-10-1994
		ZA	8903186 A	28-12-1990
		ZA	8905578 A	27-03-1991
DE 29905721	U	10-06-1999	EP	1043387 A
				11-10-2000

## CLAIMS

1. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:
  - 5 (A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and
  - 10 (B) adding an inorganic powder to a neutralization mixture in step (A) after point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A), and mixing a resulting mixture.
- 15 2. The process according to claim 1, wherein the addition of the inorganic powder is initiated in step (B) at any time between a point when the liquid acid precursor of an anionic surfactant is added in an amount exceeding a weight ratio of 0.25 to the water-soluble, alkali inorganic substance and a point up to 5 minutes from termination of addition of an entire amount of the liquid acid 20 precursor.
3. The process according to claim 1 or 2, wherein the average particle size of the inorganic powder is 30  $\mu\text{m}$  or less.
- 25 4. The process according to any one of claims 1 to 3, wherein the inorganic

powder is an alkali metal aluminosilicate.

5. The process according to claim 4, wherein the addition of the alkali metal aluminosilicate is initiated in step (B) at any time within 5 minutes from termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.
10. 6. The process according to any one of claims 1 to 5, wherein the alkali metal aluminosilicate is contained in step (A) in an amount of 5% by weight or less.
15. 7. The process according to any one of claims 1 to 6, wherein the neutralization step is carried out in step (A) while blowing a gas.
20. 8. The process according to any one of claims 1 to 7, wherein in step (B), a liquid binder is further added to the neutralization mixture obtained in step (A).
9. 10. The process according to any one of claims 1 to 8, further comprising a surface-modifying step.
25. 10. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:
  - (a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a

substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

- (b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

5

11. The process according to claim 10, wherein the addition of the alkali metal aluminosilicate is initiated in step (b) at any time within 5 minutes from termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.

10

12. The process according to claim 10 or 11, wherein the alkali metal aluminosilicate is contained in step (a) in an amount of 5% by weight or less.

15

13. The process according to any one of claims 10 to 12, wherein the neutralization step is carried out in step (a) while blowing a gas.

14. The process according to any one of claims 10 to 13, wherein in step (b), a liquid binder is further added to the neutralization mixture obtained in step (a).

20

15. The process according to any one of claims 10 to 14, further comprising surface-modifying step.

**PATENT COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference  00-020-PCT	<b>FOR FURTHER ACTION</b>		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No.  PCT/JP00/05487	International filing date (day/month/year)  17/08/2000	Priority date (day/month/year)  20/08/1999	
International Patent Classification (IPC) or national classification and IPC  C11D11/00			
Applicant  KAO CORPORATION et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I    Basis of the report
- II    Priority
- III    Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV    Lack of unity of invention
- V    Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI    Certain documents cited
- VII    Certain defects in the international application
- VIII    Certain observations on the international application

Date of submission of the demand  12/03/2001	Date of completion of this report  31.10.2001
Name and mailing address of the International preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Pfannenstein, H  Telephone No. +49 89 2399 8217



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/JP00/05487

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):  
**Description, pages:**

1-44                          as originally filed

**Claims, No.:**

1-15                          with telefax of                          06/07/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description,                  pages:
- the claims,                          Nos.:
- the drawings,                          sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/JP00/05487

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

**6. Additional observations, if necessary:**

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims
	No:	Claims 1-15
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-15
Industrial applicability (IA)	Yes:	Claims 1-15
	No:	Claims

**2. Citations and explanations  
see separate sheet**

**VII. Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP00/05487

**Re Item V**

- 1) Reference is made to the following documents:

D1 EP-A-936269  
D2 WO-A-9732003  
D3 US-A-5935923  
D4 DE-A-19735788  
D5 WO-A-9811198  
D6 EP-A-352135, cited in the application  
D7 DE-U-29905721.

- 2) The independent claims do neither comprise a particle size nor its distribution.

D1 (examples 1,11-19, claims) exemplifies a process for preparing detergent granules having a bulk density above 700 g/l, e.g in example 1 it is 760 g/l. Soda ash and tripolyphosphate are blended in a mixer, then a mixture of alkyl benzene sulfonic acid and sulphuric acid or phosphoric acid is added; no zeolite is present. After the neutralization is completed an aqueous polymer solution is added, 90 s stirred, and then, zeolite is added; i.e. within 5 min from the end of neutralization (as required in present dependent claims). The granules have an average particle size of 633 um. Thus, the subject-matter of claims 1-6, 8-12, 14-15 is not novel (Articles 33(2) PCT).

D2 (example, claims, pages 1, 6-7) describes a process for preparing high density detergent granules. In a mixer alkyl benzene sulfonic acid is neutralized by soda ash, 5,76 % zeolite is present, in a further step 1,44% zeolite is added. A value for the density is not specified. However, the process in D2 leads to high density granules. Thus it is not clear if claim 1 and D2 are really different. Furthermore, point VIII is taken into account. The subject-matter of claims 1-4, 10-11 is, therefore, not novel.

D3 (examples, claims) exemplifies a process for preparing detergent granules. In a mixer fatty acid (other anionic surfactants may be used) is neutralized by NaOH, no zeolite is present. In a further step zeolite is added. A value for the density is not specified. However, D3 (col. 3, l.38) relates to high density granules. Thus it is

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/JP00/05487

not clear if claim 1 and D3 are really different. The subject-matter of claims 1,2,4,6,8,10,12,14 is, therefore, not novel.

D4 (example, col.3) exemplifies a process for preparing detergent granules. In a mixer alkyl benzene sulfonic acid is neutralized by spraying said acid on soda ash; zeolite is not present. In a further step zeolite is added. A value for the density is not specified. However, D4 (col.3, l. 18) describes high density granules of at least 500 g/l . Furthermore, D4 (col. 3) relates to the reduction of coarse grain. Thus it is not clear if claim 1 and D4 are really different. The subject-matter of claims 1-2, 4-8, 10-14 is, therefore, not novel.

D5 (examples, claims) exemplifies a process for preparing detergent granules. In a reactor alkyl benzene sulfonic acid and fatty acid are neutralized by soda ash, no zeolite is present. In a further step tripolyphosphate is added. A value for the density is not specified. However, D5 (page 6) relates to high density granules of at least 550 g/l preferably at least 650 g/l. Thus it is not clear if claim 1 and D5 are really different. The subject-matter of claims 1-2, 4-6, 8 is, therefore, not novel. Instead of phosphate zeolite may also be used in D5 (claims). Thus the subject-matter of claims 10-12, 14 is not inventive (Article 33(3) PCT).

D6 (examples 10-14,22,24-25, claims) exemplifies a process for preparing detergent granules having a bulk density of above 700 g/l. Soda ash and tripolyphosphate are blended in a mixer, then alkyl benzene sulfonic acid is added; no zeolite is present. After the neutralization is fully or partly completed an inorganic powder such as silica, perlite, calcite is added. Thus, the subject-matter of claims 1-3, 6, 8-9 is not novel.

Aluminosilicate may also be used as an inorganic powder in D6 (claims). Thus a skilled person would arrive at claims 4-5, 10-11. Moreover, a small average particle size of the products is found in the examples. Thus the subject-matter of claims 4-5, 10-11 is not inventive.

D7 (example) also describes the process according to claims of 1-2 the application. Thus the subject-matter of claims 1-2, 7 is not novel.

**Re Item VII**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP00/05487

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the above cited documents except D6 are not mentioned in the description, nor are these documents identified therein.

**Re Item VIII**

- 1) It should be kept in mind that a claim itself should be clear (Article 6 PCT).
- 2) The problem of the present invention at page 1-2 relates to the presence of alumino silicates whereas in claim 1 alumino silicates may not be present.
- 3) Table 5 of the application shows that the detergency of comparative example 2 is as good as the inventive examples. However, there seems to be a more even particle size distribution in examples 6-9 compared to the comparison example as a result of the timing of addition of inorganic powder.
- 4) The term "substantial absence..." in claims 1 and 10 is vague and indefinite and as such renders the scope of the claim unclear; accordingly, it has not been substituted by a more precise term from the description at page 6 (Article 6 PCT).
- 5) The formulation of the point of addition of the inorganic powder in claim 1 is vague and indefinite and as such renders the scope of the claim unclear; accordingly, it has not been added by a more precise term from the description at page 14 (Article 6 PCT).
- 6) There is an inconsistency between the claims and the description. In independent claims 1 and 10 no particle size is given whereas on page 1, par. 1 "a small average particle size" is mentioned, which corresponds to at most 700 um according to page 20 (Article 6 PCT).

Furthermore, it is clear from pages 1, 13, 20 that the process should result in small particle size, which corresponds to at most 700 um according to page 20, which is essential to the definition of the invention.

Since independent claims 1 and 10 do not contain this feature they do not meet the requirement following from Article 6 PCT taken in combination with Rule 6.3(b)

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/JP00/05487

PCT that any independent claim must contain all the technical features essential to the definition of the invention. (Said feature makes claims 1 and 10 not novel over at least D1).

## CLAIMS

- REPLACED BY  
ART 34 AMDT
1. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:
    - 5 (A) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and
    - 10 (B) adding an inorganic powder to a neutralization mixture in step (A) after a point of initiation of formation of coarse grains of the neutralization mixture obtained during a course of a neutralization process in step (A) and mixing a resulting mixture.
  - 15 2. The process according to claim 1, wherein the addition of the inorganic powder is initiated in step (B) at any time between a point when the liquid acid precursor of an anionic surfactant is added in an amount exceeding a weight ratio of 0.25 to the water-soluble, alkali inorganic substance and a point up to 5 minutes from termination of addition of an entire amount of the liquid acid precursor.
  - 20 3. The process according to claim 1 or 2, wherein the average particle size of the inorganic powder is 30 µm or less.
  - 25 4. The process according to any one of claims 1 to 3, wherein the inorganic

powder is an alkali metal aluminosilicate.

5. The process according to claim 4, wherein the addition of the alkali metal aluminosilicate is initiated in step (B) at any time within 5 minutes from

5 termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.

6. A process for preparing a high-bulk density detergent composition having a bulk density of 650 g/L or more, comprising the steps of:

10 (a) blending a liquid acid precursor of an anionic surfactant with a water-soluble, alkali inorganic substance in an amount equal to or exceeding in an amount necessary for neutralizing the liquid acid precursor, in a substantial absence of an alkali metal aluminosilicate, thereby neutralizing the liquid acid precursor; and

15 (b) adding an alkali metal aluminosilicate to a neutralization mixture obtained in step (a) and mixing a resulting mixture.

7. The process according to claim 6, wherein the addition of the alkali metal aluminosilicate is initiated in step (b) at any time within 5 minutes from

20 termination of addition of an entire amount of the liquid acid precursor of an anionic surfactant.